

ARSENIC AMBIENT CONDITIONS PREVENTING SURFACE DEGRADATION OF
GaAs DURING CAPLESS ANNEALING AT HIGH TEMPERATURESC.H. Kang, K. Kondo,¹ J. Lagowski and H.C. Gatos

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ABSTRACT

Changes in surface morphology and composition caused by capless annealing of GaAs were studied as a function of annealing temperature, T_{GaAs} , and the ambient arsenic pressure controlled by the temperature, T_{As} , of an arsenic source in the annealing ampul. It was established that any degradation of the GaAs surfaces could be completely prevented providing that $T_{\text{As}}[^\circ\text{C}] \geq 0.315 T_{\text{GaAs}}[^\circ\text{C}] + 227$. This empirical relationship is valid up to melting point temperature of GaAs (1238°C) and it can be readily utilized in device processing.

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Annealing at elevated temperature is a key process step in the fabrication of GaAs integrated circuits. The temperatures between 800 and 900°C used for activation of implants are well above the congruent evaporation point (about 640°C) (1). Thus, a preferential loss of arsenic takes place during annealing. In order to prevent structural and compositional degradation of the surfaces various capping techniques have been developed which employ deposited protective films (Si_3N_4 , SiO_2 , Al_2O_3). Generation of defects during the film deposition and/or excessive interface stresses are common disadvantages of this approach (2). An alternative solution involves capless annealing in an ambient containing arsenic vapor at a partial pressure high enough to prevent decomposition of GaAs surfaces. Various sources of arsenic vapor have been proposed, i.e., GaAs powder or wafers (3,4), "melt-controlled" ambients (5,6), InAs (7,8), flowing AsH_3 (9), or a gas enriched with arsenic (10); however, no systematic quantitative study has been made on the behavior of the surface morphology as a function of the arsenic vapor pressure.

In the present study elemental arsenic was employed as a source material supplying arsenic vapor to the annealing ambient. Surfaces of GaAs crystals were examined (prior to and after annealing) by optical and electron microscopes, electron microprobe and X-ray photoelectron spectroscopy. Experimental conditions were established under which no degradation of the surface morphology and the surface composition took place upon annealing. These conditions are expressed in terms of a

relationship between the annealing temperature, T_{GaAs} , and the required temperature of the arsenic source, T_{As} .

Experimental Procedures

Annealing experiments were carried out in a closed two-zone apparatus shown schematically in Fig. 1. GaAs samples and elemental arsenic were placed in a closed quartz ampul in the hot and cold zone, respectively. They were separated by a distance of about 40 cm. The temperature of the arsenic source was precisely controlled by a sodium-filled inconel heat pipe inserted into a cold zone of the resistance furnace.

GaAs crystals employed in this study were grown by the Horizontal Bridgman (HB) and the Liquid Encapsulated Czochralski (LEC) techniques. Wafers with (100) and (111) surfaces were polished to a mirror-like finish, using a polishing solution containing 1 part of clorox bleach and 4 parts of H_2O . After polishing, the samples were cleaned in trichloroethylene, acetone and methanol. They were rinsed in deionized water and etched in concentrated H_2SO_4 and then in a stagnant solution of $3\text{H}_2\text{SO}_4 + 1\text{H}_2\text{O}_2 + 1\text{H}_2\text{O}$ for 5 min. They were rinsed again in deionized water and then etched in HCl for 5 min to remove any oxide or organic material on the surface. Finally, the specimens were rinsed in deionized water and dried with stream of nitrogen gas. Elemental arsenic of 99.9999% purity was cleaned and etched in the same way as the GaAs.

The GaAs samples and arsenic source material were placed at the opposite ends of the high purity quartz ampul, which was pre-cleaned by etching in $1\text{HF} + 1\text{HNO}_3$, washing in deionized

water and drying. The ampul was heated at 300°C for 3 h under 5×10^{-7} torr vacuum in order to accelerate the removal of residual oxides and adsorbed water. The ampul was then cooled to room temperature and sealed off under vacuum.

The annealing treatment was carried out after loading the sealed ampul into a pre-heated horizontal two-zone furnace. The annealing temperature was varied from 650 to about 1000°C, while the arsenic source temperature was varied from 400 to 620°C. The annealing time was varied from 30 min to 20 h.

The as-annealed GaAs surfaces were examined by Nomarski phase contrast microscopy. X-ray photoelectron spectroscopy (XPS) was used for the determination of the concentration ratio of [As]/[Ga] on the surface. Compositional changes on a microscale were determined by electron probe microanalysis (EPMA). In order to reveal variations on the surface with a high spatial resolution scanning electron microscopy (SEM) was carried out employing surfaces coated with carbon. The SEM apparatus was equipped with an attachment for energy dispersion X-ray analysis.

Results and Discussions

Surface degradation due to condensation of arsenic.

Upon termination of annealing the ampul is cooled down and the arsenic vapor becomes supersaturated. Condensation of arsenic on the GaAs surfaces leads to degradation of surface morphology. This degradation can be especially severe for high arsenic pressures which are required to prevent arsenic loss from the

surface during actual annealing.

Experimental results illustrating the detrimental effects of arsenic condensation are shown in Fig. 2, column (a). In this case, after annealing, the whole ampul was quenched in water to room temperature. The samples were then cleaned in HCl solution in order to remove arsenic condensed during rapid cooling; this HCl solution does not react with GaAs. The Nomarski photomicrographs shown in Fig. 2 illustrate the roughness of surfaces annealed at different T_{As} . For low arsenic source temperatures (494 and 510°C) thermal etching of GaAs takes place during annealing (due to preferential evaporation of arsenic), resulting in a poor surface quality. After passing through an optimum of $T_{As} \approx 521^\circ\text{C}$, the surface quality degrades again for higher arsenic source temperatures.

As shown in column (b) this surface degradation does not occur if the cooling is carried out so that the ampul end containing the elemental arsenic is quenched prior to quenching the end containing the GaAs; the entire quenching process is completed within a few seconds. Under such conditions most of the arsenic vapor condense on the inside ampul wall of the arsenic source zone, and the GaAs surfaces are not contaminated with arsenic. Photomicrographs shown in column (b) correspond to "as-annealed" surfaces without cleaning in HCl which was used for the surfaces shown in column (a).

Surface stability range.—When the detrimental effects of arsenic condensation during post-annealing cooling are eliminated, the surface quality remains very good for high arsenic source temperatures. However, deterioration of the

surfaces always takes place for low T_{As} values. Nomarski phase contrast micrographs of GaAs annealed at 800°C for 16 h under different T_{As} values are shown in Fig. 3. T_{As} of 440, 470 and 475°C yielded poor quality surfaces, while $T_{As} = 480, 490$ and 520°C yielded surfaces of good quality. We performed a series of such annealing experiments; the results are summarized in Fig. 4 in the form of a pressure-temperature diagram. For each annealing temperature the arsenic source temperatures yielding poor quality surfaces are marked with filled circles, while open circles correspond to good quality surfaces.

The borderline drawn between filled and open circles separates the regions of good and bad surface morphology. It is of interest to note that the borderline passes through the point $T_{GaAs} = 1238^\circ\text{C}$ and $T_{As} = 617^\circ\text{C}$ which corresponds to melting point equilibrium conditions for GaAs with optimum stoichiometry (11).

Arsenic pressure values given in Fig. 4 represent the total arsenic vapor pressure in equilibrium with solid arsenic at temperature T_{As} . These values are adopted from ref. 12.

The borderline separating good and bad morphologies is shown in Fig. 5 in linear T_{GaAs} and T_{As} coordinates. The line represents the critical arsenic source temperature, T_{As}^C , and is described by

$$T_{As}^C [^\circ\text{C}] = 0.315 T_{GaAs} [^\circ\text{C}] + 227. \quad [1]$$

Stable surfaces with good morphology are obtained for $T_{As} \geq T_{As}^C$, while for lower arsenic source temperatures, $T_{As} < T_{As}^C$, surface degradation takes place associated with preferential evaporation of arsenic.

Changes in surface composition.—The XPS spectra shown in Fig. 6 illustrate annealing-induced changes in the surface concentration of gallium and arsenic. Surfaces annealed under low arsenic source temperature (spectra A) exhibit a low intensity As 3d peak and a pronounced Ga 3d peak. This behavior is consistent with preferential arsenic evaporation and the resulting enrichment of the surface with gallium. Spectra B and C correspond to annealing with $T_{As} \approx T_{As}^C$ and $T_{As} > T_{As}^C$, respectively. It is seen that indeed under these conditions the surfaces remain stable with the As to Ga concentration ratio equal to approximately one. The XPS spectra were taken on "as-annealed" surfaces. It is thus not surprising that they show an additional peak corresponding to arsenic oxide formed probably as a result of exposure to air after annealing. Ta-related peaks in the vicinity of the Ga 3d peak originate from the specimen holder in the XPS apparatus.

SEM measurements showed that surfaces of GaAs annealed under low arsenic pressure ($T_{As} < T_{As}^C$) contained microscopic inhomogeneities in the form of droplets about 1 μ m in diameter (see Fig. 7). Energy dispersive X-ray spectra shown in the lower portion of Fig. 7 show that the inhomogeneous regions (droplets) correspond to enhanced Ga to As concentration ratio. The linear microscan of an X-ray intensity profile of the Ga K α and As L α lines, respectively, presented in Fig. 8 also shows spatial variations (opposite in phase) of Ga and As concentrations on surfaces annealed with $T_{As} < T_{As}^C$. No such variations were detected on surfaces annealed with $T_{As} > T_{As}^C$.

Our findings on the compositional and morphological

changes of GaAs annealed under different arsenic pressures closely resemble the surface behavior in molecular beam epitaxial (MBE) growth of GaAs (13). Two surface stability regions are considered in MBE, namely, As-stabilized surfaces for high As/Ga flux ratio and relatively low temperatures, and Ga-stabilized surfaces low As/Ga flux ratio and relatively higher temperatures. These results can complement ours, provided two main differences are taken into consideration. One is that the annealing temperature in our study is higher than the typical growth temperature in MBE (usually about 600°C). The other is that only the arsenic flux (controlled by T_{As}) is employed in our experiments.

MBE studies (14,15) have shown that if a monolayer of gallium is present on the surface, the sticking coefficient of arsenic is unity. As the surface gallium atoms are consumed through the interaction with incident arsenic atoms, the sticking coefficient of arsenic decreases, and finally equilibrium composition of the GaAs surface is achieved. Arsenic atoms which do not form bonds with gallium simply desorb from the surface. In our case, no gallium flux is employed and consequently conditions of equilibrium surface compositions are easily attained as long as $T_{As} > T_{As}^C$. Below the equilibrium arsenic pressure, the GaAs surface remains Ga-stabilized for the whole annealing period. Moreover, prolonged annealing causes gallium-rich droplets to develop on the GaAs surface as shown in Fig. 7. When the GaAs crystals are annealed with $T_{As} > T_{As}^C$, excess arsenic atoms remain in the ambient and the equilibrium

stoichiometry is maintained on the GaAs surface during annealing.

The presently determined equilibrium arsenic pressure data can be readily utilized in actual GaAs device processing. By annealing GaAs under arsenic pressures above equilibrium, the as-annealed GaAs wafers of undegraded surface can be directly transferred to the next steps in the processing without any further surface treatments.

Conclusions

It was determined that, during high temperature capless annealing, the surface morphology of GaAs undergoes no detectable changes under ambient arsenic pressure higher than a critical value. This annealing temperature-dependent minimum arsenic source temperature (and thus the minimum arsenic pressure) corresponds to the gas phase equilibrium with stoichiometric GaAs surface at the annealing temperature. The critical arsenic source temperatures were determined for various annealing temperatures, and they can be readily utilized in actual GaAs device processing.

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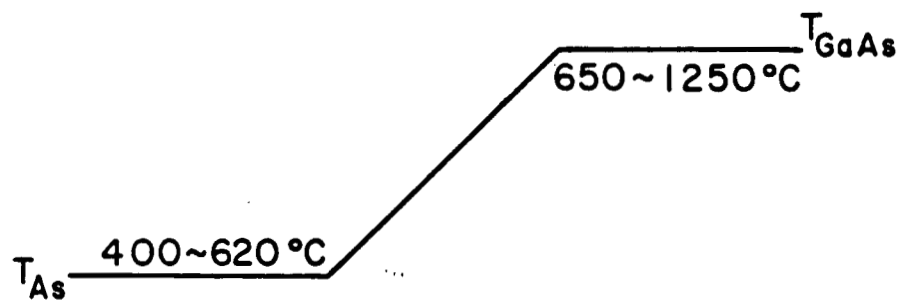
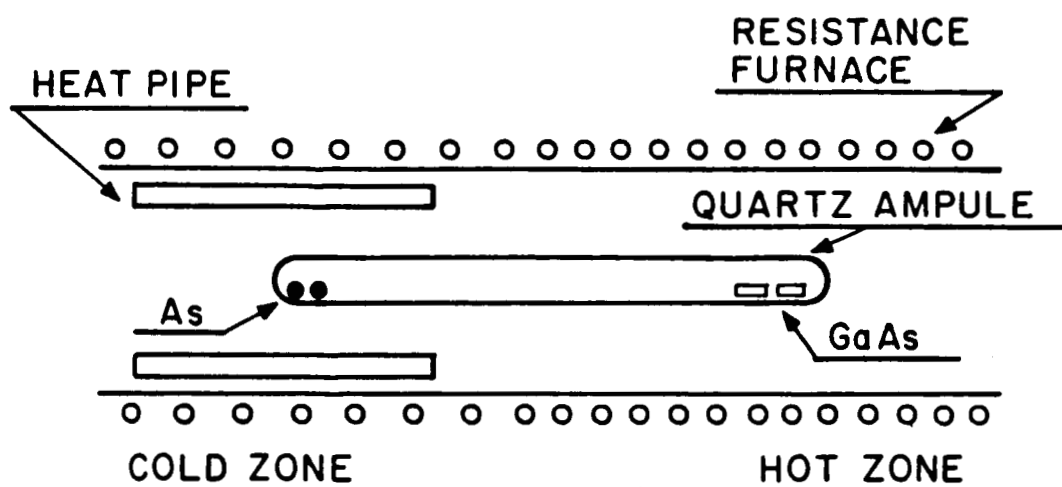
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FIGURE CAPTIONS

- Fig. 1. Two zone apparatus employed for annealing of GaAs and corresponding temperature profile.
- Fig. 2. Photomicrographs of GaAs surfaces after 900°C annealing for 16 h with different arsenic source temperatures. Column (a)——arsenic source and GaAs were cooled simultaneously; column (b)——arsenic source was quenched first.
- Fig. 3. Nomarski micrographs of surfaces of GaAs annealed at 800°C for 16 h with different temperatures of arsenic source. (Arsenic source was quenched first.)
- Fig. 4. Pressure-temperature diagram of GaAs showing the arsenic pressures which yield poor (filled circles) and good (open circles) surface morphologies at different annealing temperatures. The equilibrium arsenic pressure value at each arsenic source temperature was adopted from ref. 12.
- Fig. 5. The linear relationship between annealing temperature (T_{GaAs}) and arsenic source temperature (T_{As}) for the borderline separating good and bad surface morphologies in Fig. 4.
- Fig. 6. XPs spectra of Ga 3d and As 3d peaks for the GaAs annealed at 700°C for 16 h with arsenic source temperatures of (A) 415°C, (B) 450°C, and (C) 470°C.
- Fig. 7. Scanning electron micrograph of the GaAs surface annealed at 750°C for 16 h with $T_{\text{As}}=440^\circ\text{C}$ and energy dispersive X-ray spectra obtained at the dark droplet

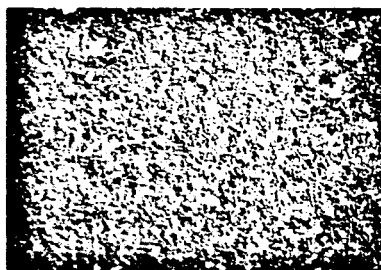
(a) and the bright matrix (b).

Fig. 8. X-ray intensity profiles of Ga $K\alpha$ and As $L\alpha$ in the middle section of the micrograph in Fig. 7.

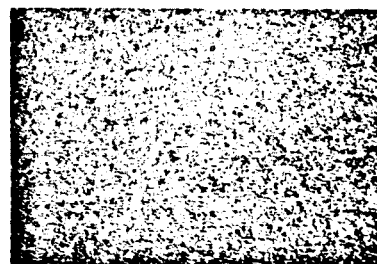
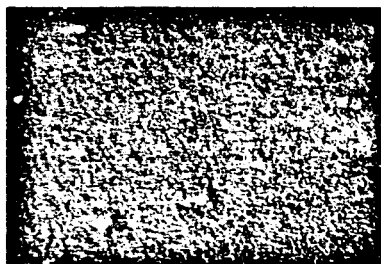


T_{As}

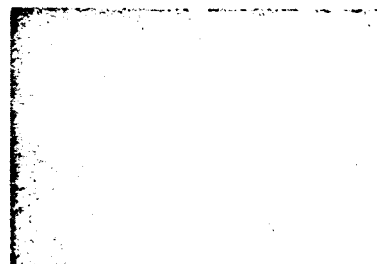
494°C



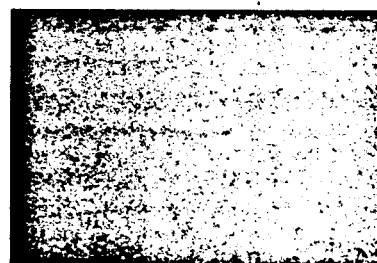
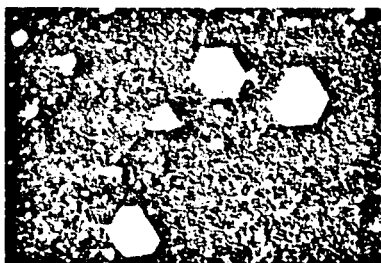
510°C



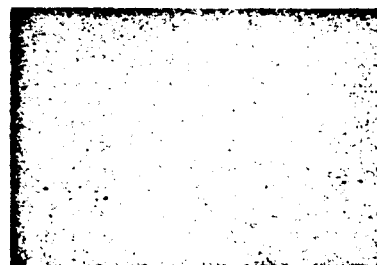
521°C



530°C



541°C



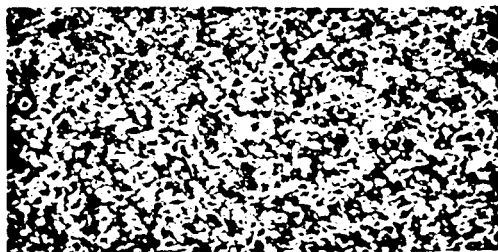
(a)

200 μ m

(b)

DEGRADED SURFACES

200 μm

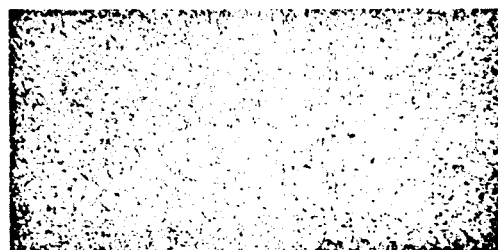


T_{As}

440 °C



470 °C

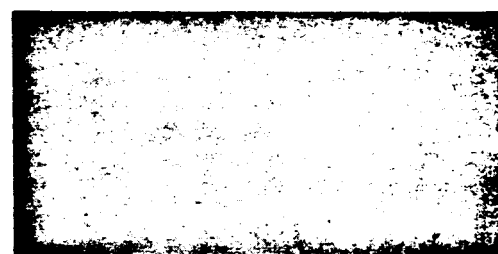


475 °C

← GOOD QUALITY SURFACES →

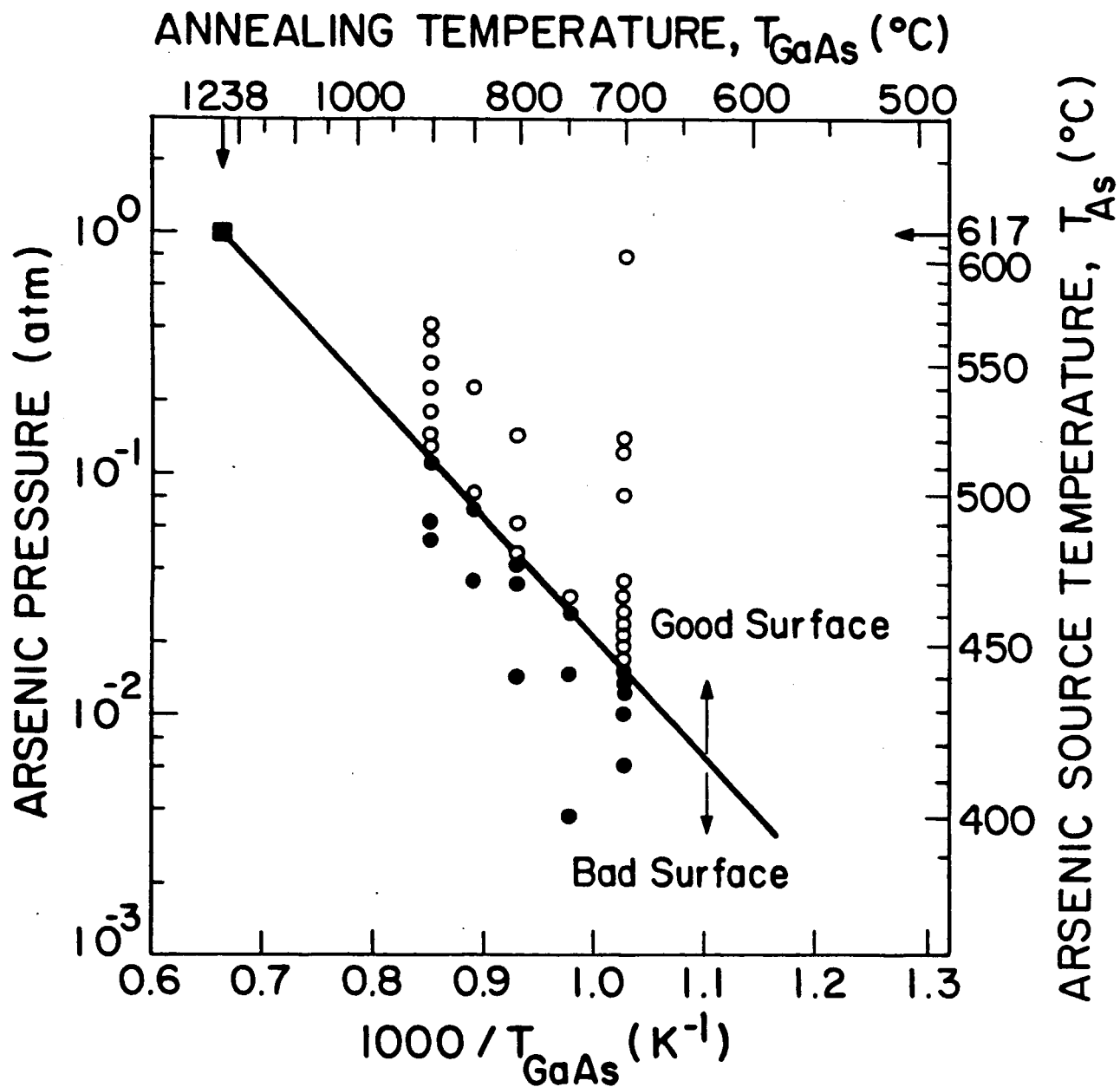


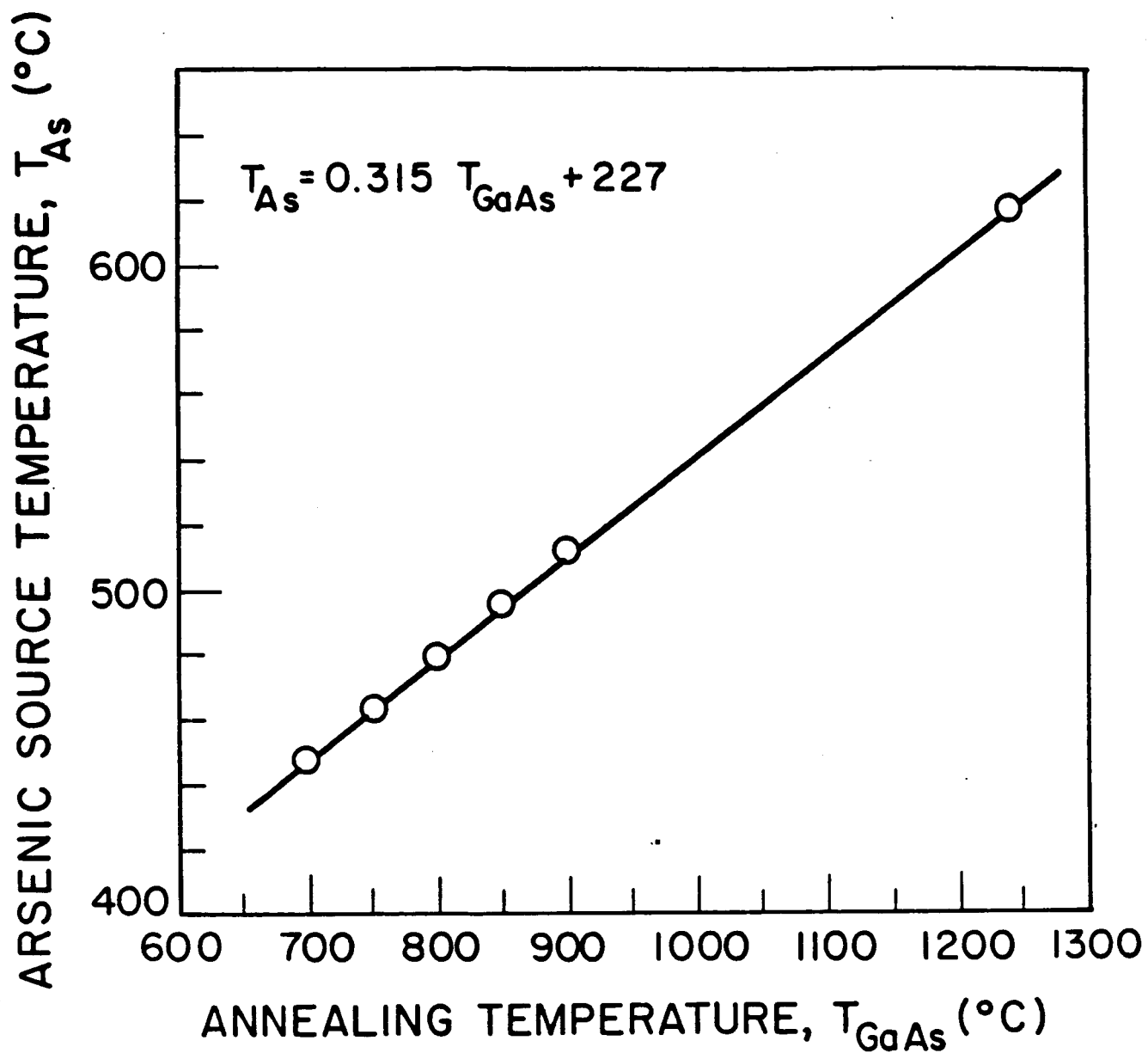
480 °C

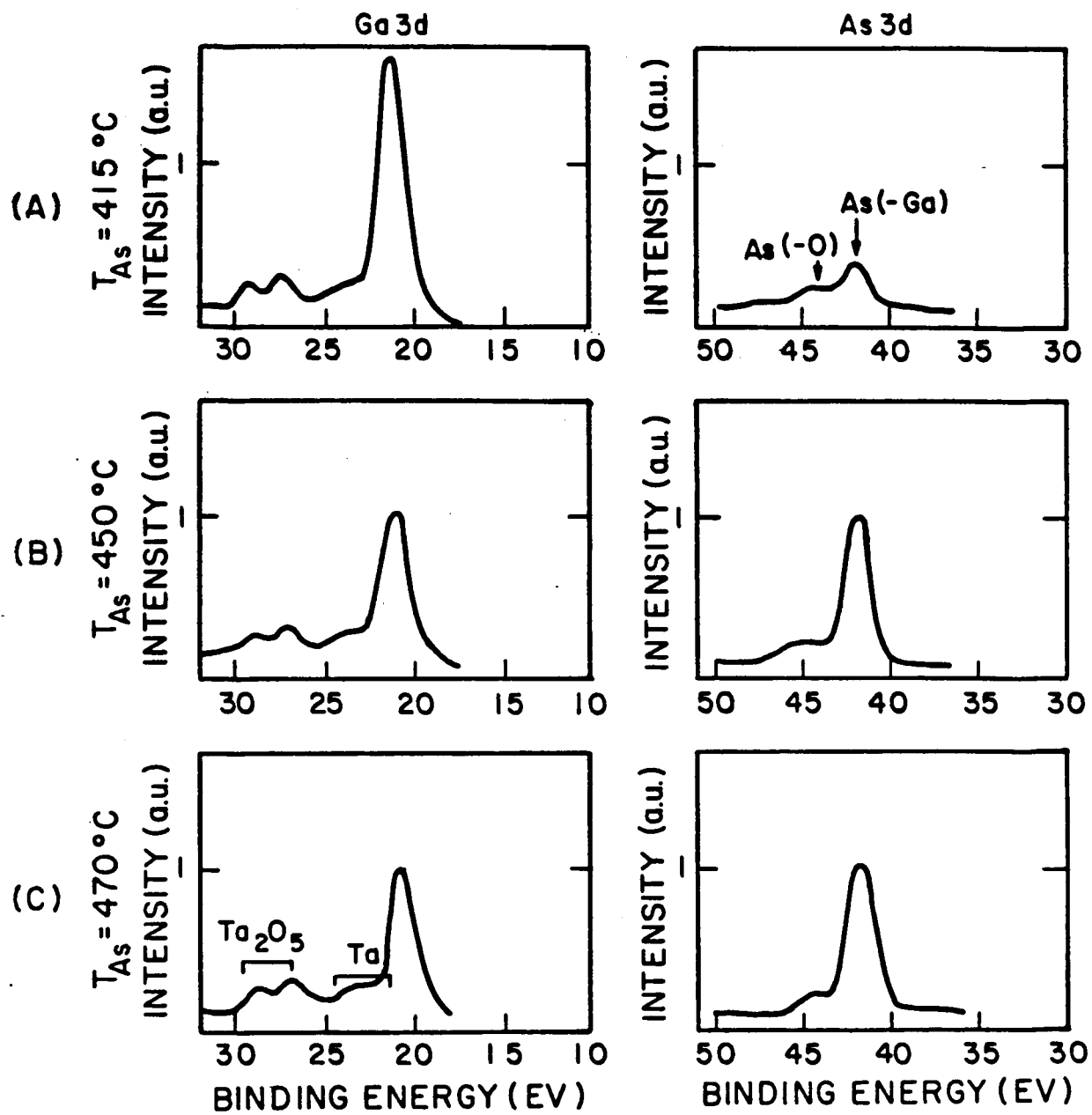


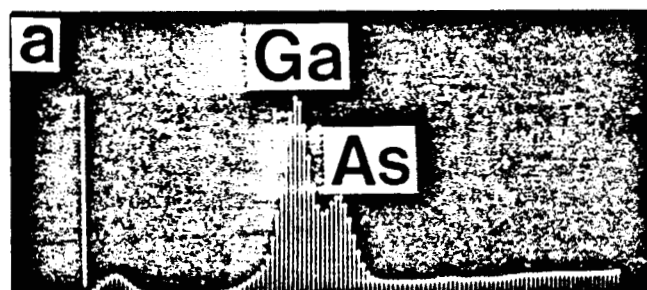
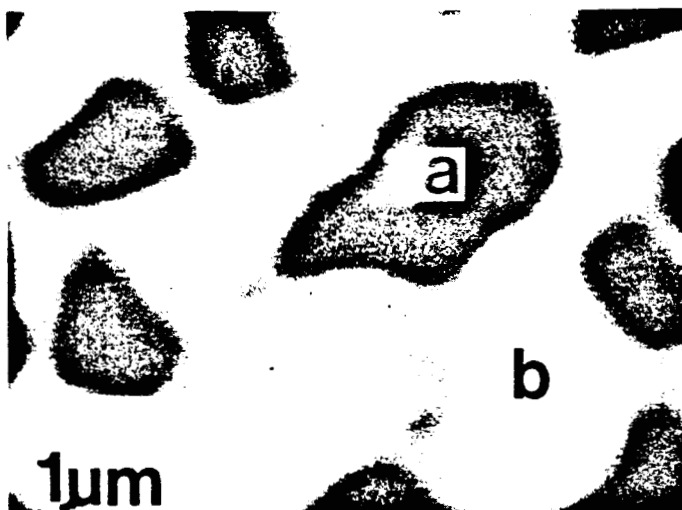
490 °C

520 °C









ENERGY



ENERGY

